Methods for the Stable Isotopic Analysis of Chlorine in Chlorate and Perchlorate Compounds

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Chlorate and perchlorate compounds, used as herbicides, solid fuel propellants, and explosives, are increasingly recognized as pollutants in groundwater. Stable isotope characterization would permit both environmental monitoring of extent of remediation and forensic characterization. Stoichiometric reduction to chloride (greater than 98% yield), by Fe(II) for chlorate and alkaline fusion–decomposition for perchlorate, allows analysis by standard methods to give highly reproducible and accurate δ^{37}Cl results (0.05‰, 2 × standard error). Analysis of various compounds from different suppliers yielded δ^{37}Cl values for chlorate samples near to +0.2‰ (SMOC), but one has within-sample heterogeneity of 0.5‰, possibly due to crystallization processes during manufacture. Results for perchlorate samples also are generally near +0.2‰, but one is +2.3‰ (SMOC). The initial results suggest that both forensic and environmental applications might be feasible.

Chlorate and especially perchlorate are almost totally manmade. The compounds manufactured include sodium and potassium chlorate ($NaClO_3$, $KClO_3$) and the sodium, potassium, and ammonium perchlorate salts ($NaClO_4$, $KClO_4$, NH_4ClO_4). Chlorates have two principal types of use: as weed-killers and, together with perchlorates, as oxidants in explosives and solid fuel rockets. Criminal misuse of explosives presents a potentially grave threat to the safety and welfare of the public. To meet this threat, the Forensic Explosives Laboratory (FEL) provides a forensic service to U.K. police forces to assist the investigation and prevention of such crimes. Thus, there is a forensic interest in tracing their sources. Chlorate and perchlorate are produced as pure salts; therefore, chemical composition is of little use as a tracer. However, chlorine stable isotope analysis has the potential of providing forensic evidence of high probative value, for example, by linking or distinguishing between explosive traces found on an individual and a specific bulk or explosive traces found at a number of locations.

Perchlorate (especially the ammonium salt) is used in solid fuel missiles, rocket engines, fireworks, and, more recently, in car air bags. However, especially as a result of military use and despite usually careful disposal, perchlorate has been released to groundwater systems as a result of decommissioning missiles.[1] As a consequence of high solubility, perchlorate (and to some extent chlorate) can be a localized significant pollutant of drinking water.[1] Concentrations of perchlorate, measured in water supply wells, are usually at the level of tens or hundreds of ppb but can approach or even exceed 1 ppm. Perchlorate can release iodide from the thyroid gland and was used for treatment of Graves disease. However, in general, it will produce effects similar to iodine deficiency, whereby impaired production of thyroid hormones causes problems to the normal development of embryos and infants.[2,3] Therefore, its presence in water clearly gives rise to concern as to its effects as a health hazard and also as an ecotoxicological agent.

Remediation of perchlorate pollution potentially can be accomplished by bacterial reduction,[4] and, if it occurs through indigenous bacteria (intrinsic remediation), requires only repeating monitoring to gauge the progress of the process. Bacterial processes may impart a large isotopic fractionation affecting both the product and the residual pollutant; thus, their isotopic compositions may be used to measure the extent to which the remediation process has progressed.[5]

Thus, in all these cases, there is potential value in being able to use chlorine stable isotope compositions to characterize chlorate and perchlorate sources either environmentally or in terms of producer/batch and to monitor its destruction in the environment.

Measurements are made using a stable isotope ratio mass spectrometer. Seawater has been used as the standard since Kaufmann et al.[6,7] proved that the chlorine isotopic composition of seawater was constant. They called this Standard Mean Ocean Chloride (SMOC); no formal isotopic standard has been prepared so far. In this study, all measurements are given with respect to the seawater Atlantic 2, a laboratory reference material sampled in the Gorringe Sea. Our measurements and those of others[8] have shown no measurable isotopic differences between this seawater and any others.

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For all elements, the relatively larger isotopic fractionations result from energetic chemical reactions that change redox or pH state and thus have larger differences of bond strength between sites in equilibrium with each other. In low-temperature (<50 °C) natural systems, chlorine is not involved in such chemical reactions, and most of the measured values for $\delta^{37}Cl$ are very close to the value of seawater, 0‰. With few exceptions, the range of variation of chlorine isotopic composition in sedimentary material is very small (classically from −2 to +1‰ SMOC). Exceptions to this small range of variation are deep subsurface brines associated with oil reservoirs, which may have values as low as −5‰,[9] or fluid expelled by mud volcanoes along tectonic plate subduction zones.[8] Thus, most natural sources of chloride in natural environments at risk from pollution have a characteristic small range of chlorine isotope composition. Especially, ancient as well as modern evaporites (most probably used as feedstock for the chlorate and perchlorate production) have been shown to have a $\delta^{37}Cl$ value of -0.09 ± 0.37‰.[8]

In the case of chlorate and perchlorate, energetic chemical reactions with important changes in redox potential occur during the process of oxidation of chlorine. These changes in redox potential have the possibility of imposing isotopic fractionation on the feedstock chlorine. Variations in conditions and reaction pathways of synthesis processes may give differences in isotopic compositions of manufactured compounds, as shown by Jendrzejewski et al.[10] in the case of trichloroethene, which gave a range of $\delta^{37}Cl$ values of 2.6‰ for different manufacturers.

From the point of view of remediation of chlorate and perchlorate pollution, there is the possibility that microbial degradation of these compounds might produce a significant isotopic fractionation of chlorine isotopes, as shown by Coleman et al.[5] for chlorinated hydrocarbon solvent degradation. Monitoring the extent of intrinsic (natural) remediation could then be achieved by measuring isotopic compositions of residual chlorate or perchlorate and chloride produced.

Although there are established methods to determine $\delta^{37}Cl$ of chloride,[11] so far no method has been published for the isotopic analysis of chlorine in chlorate and perchlorate. To do so, we chose to convert chlorate and perchlorate to chloride so that the standard method could then be applied. We used old and well-established chemical analysis methods for quantitative reduction of chlorate and perchlorate to chloride.

EXPERIMENTAL SECTION

Methods for the quantitative analysis of chlorate and perchlorate have been developed since the beginning of the last century. They rely on quantitative conversion of chlorate or perchlorate to chloride and gravimetric measurement of chloride as silver chloride. Chlorate solution is heated with ferric iron,[12] and perchlorate salts are fused at 600 °C with potassium carbonate.[13] Repeated tests showed that both these methods are reliable and blanks are negligible. The method for chlorine isotope analysis also requires chlorine in the sample to be converted to silver chloride. Subsequently, the silver chloride must be reacted stoichiometrically with excess iodomethane. The resultant chloromethane is separated from residual iodomethane by gas chromatography before introduction to the mass spectrometer. In the absence of chlorine isotope standard materials for chlorate and perchlorate, checking that these preparation methods are valid for isotopic analysis purpose requires that rigorous criteria be adopted. The replicate results must be reproducible, conversion yields should be near to 100%, and there should be negligible blanks. If these criteria are met, then it is reasonable to assume that the chlorine analyzed is exactly the same as that in the original material and, thus, has its isotopic composition.

Quantitative Reduction of Chlorate to Chloride. The chlorate was quantitatively reduced to chloride by warming with excess of iron(II) in the presence of a relatively high concentration of sulfuric acid, following step by step the procedure for quantitative analysis of chlorate given by Vogel.[12] We proceeded as follows, 2.5 mL of a 0.2 M ammonium iron(II) sulfate solution in 2 M sulfuric acid and 1 mL of concentrated sulfuric acid were added to 2.5 mL of a 0.02 M chlorate solution. The mixture was heated at 80 °C for 10 min and allowed to cool to ambient temperature.

Quantitative Reduction of Perchlorate to Chloride. Two methods proposed in the literature for the quantitative reduction of perchlorate to chloride were tried. One method[14] is similar in approach to that taken for chlorate reduction. A 2-mL aliquot of a titanium sulfate (15%) solution and 1 mL of concentrated sulfuric acid were added to 2.5 mL of a 0.02 M perchlorate solution. The mixture was heated at 100 °C for 15 min and allowed to cool to ambient temperature. These steps are to be done under a nitrogen flux, Ti(III) being oxidized when in contact with air.

The other method is adapted from Joan and Reedy.[13] The perchlorate solution is made alkaline with potassium carbonate (~300 mg of K_2CO_3 for 50 μmol of ClO_4) and evaporated to dryness in a nickel crucible. The later is then placed in a muffle furnace, heated to 600 °C (for 45 min), and then cooled to ambient temperature. Distilled water (between 20 and 50 mL for 300 mg of K_2CO_3) is added to the resulting salt until its complete dissolution. The solution is then acidified until the pH is lower than 3 (between 0.3 and 0.5 μL of nitric acid concentrated at 69%) and treated in the normal way for chlorine isotopic analysis.

Precipitation of Silver Chloride. A 4-mL aliquot of 1 M KNO_3 solution and 2 mL of a Na_2HPO_4–citric acid buffer solution are added to the chloride solution to give an ionic strength and pH suitable for precipitation of uniformly small silver chloride crystals needed for the next stage of the process. The mixture is heated to ~80 °C and 1 mL of 0.2 M $AgNO_3$ solution is added to precipitate AgCl.

Analyses of a Mixture of Perchlorate or Chlorate with Chloride. There is a problem with using the normal procedure for analysis of mixtures. The huge quantities of nitrate added for normal precipitation of chloride would oxidize the iron(II) necessary for the reduction of chlorate, and heating citric acid with perchlorate would be potentially hazardous. Therefore, precipita-

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Table 1. Sample Description

sample code	material	supplier
A	potassium perchlorate reagent	BDH Chemicals
B	sodium perchlorate reagent	Fison Scientific Apparatus Ltd
C	potassium perchlorate reagent	Fisher Scientific
D	potassium chlorate	M&B Ltd lot 18638
E	sodium chlorate reagent	BDH Chemicals batch 1
F	sodium chlorate reagent	BDH Chemicals batch 2
G	sodium chlorate "weed killer"	Doff

tion of silver chloride was performed by using a modification of the normal procedure, adding just nitric acid (50 μL in 5 mL of solution) and silver nitrate. Silver chloride is removed by filtration in the normal way; the filtrate is concentrated by evaporation before being reacted as described above, but away from the daylight, for chlorate or perchlorate reduction

Determination of the Cl Isotope Composition. δ^{37}Cl was determined by mass spectrometry, measuring the ratio of masses 52 ($CH_3{}^{37}Cl^+$) and 50 ($CH_3{}^{35}Cl^+$).[11] All samples are measured on a VG SIRA 12, triple-collector, dual-inlet, isotope ratio mass spectrometer. Samples of seawater chloride reference material were run as samples with each batch of analyses.

Determination of the Chloride Yields and Blanks. The chloride yield and blanks could not be measured directly by gravimetry (weight of the silver chloride precipitate) in the case of chloride produced by chlorate and perchlorate reduction, because the final solutions contain compounds other than silver chloride (mostly oxides) which are retained on the filter. Three other, different assay methods were used.

The yield was measured by comparison of the CH_3Cl peak area given by gas chromatography for the sample to that for seawater standards of known size. However, this calibration depends on the precision of chloride concentration measurement in the seawater The relative precision for this method varies between ±5 and ±10%. The chloride blanks were assessed using the intensity of the mass spectrometer signal of the major ion beam (mass 50). For quantitative reduction of perchlorate, the chloride blanks and the chloride yields were also assessed by ion chromatography, using a Dionex AG11 guard column and a Dionex AS11 separator column and eluant.

Safety Considerations. Most of the safety considerations are linked to the use of strong acid: manipulation and heating of the acid solutions were performed in a fume cupboard. Special care was taken to ensure that the evaporated perchlorate solutions were free from organic contamination before they were heated to 600 °C. Any possible organic contamination in the crucible was removed by combustion at 700 °C prior to its use. The crucibles were covered with aluminum during the evaporation to dryness to prevent any possible organic dust from falling in.

RESULTS AND DISCUSSION

Samples Analyzed. Only a small selection of materials was used for these investigations, consisting mainly of laboratory reagents and one sample of herbicide, sodium chlorate (Table 1). The initial tests for reproducibility of the isotopic composition and yield by gas chromatography peak area were performed on multiple aliquots of freshly prepared solutions of BDH potassium perchlorate (A1, A2, A3) and M&B potassium chlorate (D1) The test for the reproducibility of the yield and blank by ion chromatography were performed on multiple aliquots of a freshly prepared solution of Fisons sodium perchlorate (B1). Solutions were used to ensure homogeneity of sample and thus identical compositions of subsamples. Subsequently, solid subsamples were analyzed to investigate intersample and intrasample heterogeneity.

Table 2. Ion Chromatography Analysis of Chloride, Chlorate, and Perchlorate in Unreacted and Reacted Aliquots of the Fison Sodium Perchlorate Solution B1

	ClO_3 (ppm) ±5% rel	ClO_4 (ppm) ±5% rel	Cl (ppm) ±5% rel	Cl yield (%)
unreacted B1	<0.1	328	<0.1	
reacted B1				
aliquot 1	<0.1	<1	60.5	97.4
aliquot 2	<0.1	<1	60.2	96.9
aliquot 3	<0.1	<1	60.7	97.7
aliquot 4	<0.1	<1	61.5	99.0
aliquot 5	<0.1	<1	61.3	98.6
mean				97.9
σ				0.9

Blanks. Blanks were prepared for the whole process of chlorate or perchlorate reduction and also on the unreacted solutions of the chlorate and perchlorate samples. The products of these tests were compared with the blank for chloride precipitation alone using the most sensitive method, mass spectrometry. Using the usual gas introduction technique, blanks give a maximum signal of 4×10^{-13} A, whereas a sample of 60 μmol (normal size) gives a mean signal of 2800×10^{-13} A. Making the assumption that the intensity is approximately proportional to the amount of chloride, the blanks can be assessed; they are lower than 0.1 μmol. The fact that there is no measurable difference between these different blanks implies that there is no measurable blank in the chemical products used (reagent or samples) and that the blank comes from the distilled water. Since the blank is the same for standards as for samples, and because it represents less than 0.1% of the sample mass, corrections for the blank were not necessary.

Reaction Yield. The titanium method,[14] although very useful with respect to quantification of perchlorate by back-titration of the excess titanium(III), proved useless with respect to the quantitative conversion to chloride. Conversion yields estimated either by IC or by gas chromatography traces were not reproducible and ranged from 0 to 90%. We therefore used this method only for assay and tried the alkaline fusion method for isotopic analysis purposes.

For the alkaline fusion method,[13] ion chromatography results show that the conversion of perchlorate (solution B1) to chloride is quantitative (Table 2): perchlorate left in the sample is below the detection limit, and an apparent 97.9 ± 0.9% (1σ) of the perchlorate is turned into chloride. Because there is no perchlorate left in the sample, this yield of slightly lower than 100% can be explained either by impurity of the perchlorate sample, despite its claimed greater purity, or by an inaccuracy in the only measure of the perchlorate concentration of the unreacted solution (Table 2).

Chloride yields estimated using the gas chromatograph peak areas are very similar for chlorate and perchlorate solutions:

Table 3. Standard Seawater, Chlorate, and Perchlorate Solution Stable Chlorine Isotopic Composition Analysis To Test Reproducibility

	reference chloride		perchlorate (BDH)	
solution	yield (%)	δ^{37}Cl (‰)	yield (%)	δ^{37}Cl (‰)
A1	104	−0.01	100	+0.36
A1	96	+0.05	99	+0.31
A1	nd	−0.03	87	+0.31
A2	97	+0.01	96	+0.33
A2	91	−0.01	102	+0.22
A2	112	+0.00	98	+0.35

	reference chloride		perchlorate (BDH) mixed with seawater Cl^-		seawater Cl^- separated from perchlorate	
solution	yield (%)	δ^{37}Cl (‰)	yield (%)	δ^{37}Cl (‰)	yield (%)	δ^{37}Cl (‰)
A3	98	+0 06	102	+0.34	nd	−0.03
A3	nd	−0.01	103	+0.38	91	+0.03
A3	102	+0 02	98	+0.25	92	+0.01
A3	97	−0 05	102	+0.33	91	+0.02
mean	99.6	0.00	98.7	+0.32	91.6	+0.01
σ	6.4	0.04	4.7	0.05	0.7	0.03
2SE	4.5	0.03	3.4	0.04	0.5	0.02

	reference chloride		chlorate (M&B)	
solution	yield (%)	δ^{37}Cl (‰)	yield (%)	δ^{37}Cl (‰)
D1	88	−0.02	103	+0.36
D1	111	−0.01	94	+0.18
D1	101	−0.02	108	+0.13
D1	102	+0.04	90	+0.15
D1	98	+0.01	97	+0.19
D1			95	+0.28
mean	100	0.00	97.9	+0.22
σ	8.3	0.03	6.6	0.09
2SE	5.9	0.02	4.6	0.06

respectively, 97.9 ± 6.6 and 98.7 ± 4.7% (1σ) (Table 3). These relatively low yields are more likely to reflect an inaccuracy in the determination of the seawater Cl concentration than an incomplete reduction of chlorate or perchlorate. The gas chromatograph was calibrated by using the concentration of a reference seawater Cl^- material that gave values of 21 150 ppm: average of two independent determinations, one by potentiometric titration giving 20 245 ppm and one by HPLC giving 22 052 ppm.

Isotopic Analysis Reproducibility Test. For the titanium(III) method,[14] the isotopic composition of the chloride recovered was, as expected, not reproducible. It varied between −1.8 and −9.5‰, demonstrating its unsuitability for isotopic analysis. The chlorine stable isotopic analytical precision for perchlorate reduced by alkaline fusion was determined on three samples of each of two solutions of 0.02 M BDH potassium perchlorate (samples A1 and A2) and four samples of a third solution of BDH potassium perchlorate mixed with some standard seawater as a source of chloride (sample A3). Results are shown in Table 3. As mentioned in the Experimental Section, samples of isotopic reference chloride (seawater) were run with each batch of analyses. For comparison of precision of analysis, the values of seawater reference chloride run with each batch are given in the third column of Table 3. The value of δ^{37}Cl for the perchlorate solution is +0.32‰, and

Table 4. Within- and Between-Sample Chlorine Isotope Heterogeneity of Sodium Chlorate

sample code	description (5 ± 2 mg)	δ^{37}Cl ± 0.05‰
E, BDH, batch 1	10 big crystals	+0.42
	small crystals	+0.11
	small crystals	−0.11
F, BDH, batch 2	3 big crystals	−0.09
	13 medium crystals	−0.21
	small crystals	−0.34

Table 5. Between-Sample Chlorine Isotope Variability of Chlorate and Perchlorate

samples	no. of lyses	δ^{37}Cl (‰)	σ
M&B $KClO_3$	6	+0 22	0.09
DOFF $NaClO_3$	2	+0.26	0 03
BDH $KClO_4$	10	+0.32	0 05
Fisher Scientific $KClO_4$	3	+0.23	0.05
Fison $NaClO_4$	3	+2.30	0 10

the reproducibility of the whole perchlorate method (including reduction to chloride) is 0.05‰ (1σ) for the 10 samples. All 10 samples were included in the mean value since there is no significant difference between the mean of pure perchlorate sample values (+0.31‰) and that of those separated from chloride (+0.33‰). δ^{37}Cl for chlorate reduced by iron(II) was determined on six samples of 5 mL from the same 0.02 M solution of M&B potassium chlorate (sample D1). The mean value of δ^{37}Cl for the chlorate solution is +0.22‰, and the reproducibility of the whole chlorate method (including reduction to chloride) is 0.09‰ (1σ) for the six samples.

Analyses of a Mixture of Perchlorate with Chloride. Analysis of a mixture of chloride and perchlorate was tested using a perchlorate solution mixed with standard seawater (solution A3 in Table 3). The δ^{37}Cl of the chloride, precipitated with nitric acid and silver nitrate, and the δ^{37}Cl of the perchlorate have the same isotopic compositions as, respectively, the standard seawater and the perchlorate prepared independently in the normal way.

Test Application. In addition to samples used for the development of the methods, two samples of pure chlorate (different batches from the supplier BDH), one sample of weed killer (DOFF) containing a mixture of chloride and chlorate, and two samples of pure perchlorate (different suppliers) were analyzed. The descriptions are listed in Table 1. The heterogeneity of chlorine stable isotope compositions of single samples of pure chlorate as well as the variation of chlorine stable isotope compositions between different containers was investigated. The results are reported in Tables 4 and 5.

For batches of ~5 mg of crystals of different sizes in samples E and F, there are variations of the δ^{37}Cl of up to 0.5‰: the bigger the crystals, the higher their δ^{37}Cl (Table 4). There are also bulk differences between these two samples, the δ^{37}Cl of both the big and small crystals being more positive for sample E than for sample F. The other two chlorate samples analyzed do not show significant differences in their bulk δ^{37}Cl values and they belong to the range of δ^{37}Cl of big and small sample E crystals (−0.09 to +0.45‰). Unfortunately the crystals of the perchlorate

samples analyzed are too small to assess the variability of the $\delta^{37}Cl$ in crystals from the same batch. However, analysis of different perchlorate samples showed that major differences can be found, the $\delta^{37}Cl$ values being +0.15 and +0.33‰ for potassium perchlorate and +2.4‰ for sodium perchlorate (Table 5).

DISCUSSION

Replicate analyses showed that both the alkaline fusion method for perchlorate and the iron reduction methods for the chlorate are reliable. The chlorate and perchlorate reduction is complete, the yield of chloride is close to 100%, and the blanks are negligible. The reproducibility of the isotopic analysis for perchlorate is ±0.05‰ (1σ), and for chlorate 0.09‰ (1σ). These methods can be used with confidence for the isotopic analysis of the chlorine stable isotopic compositions of chlorate and perchlorate.

The variations found in this initial test application are also of interest. During crystallization of a compound from solution, one would normally expect there to be an isotopic fractionation between solution and solid. Since the heavier isotope is preferentially partitioned into the site with stronger bond energy, the solid usually has a more positive isotope value. This was demonstrated in the particular case of precipitation of halite from NaCl solution by Eggenkamp et al.[15] The solution is therefore left relatively depleted in the heavier isotope, which implies that smaller crystals that nucleated later and did not grow as long as the bigger ones, as well as outer zones of crystals, should have more negative isotope values. This isotopic effect associated with crystallization is probably at least partly responsible for the differences in the isotopic composition of chlorine observed between crystals of sodium chlorate in a single batch.

Superimposed on this internal variability (in the chlorate at least), there are significant differences between the measured isotopic compositions of chlorine in the chlorate and perchlorate samples analyzed. These indicate possible differences in source of chlorine or manufacturing process.

It is of interest to note that the measured values are different from those expected of the most probable feedstock chloride marine evaporites which have a mean $\delta^{37}Cl$ of +0.09‰[8] This suggests that the manufacturing process does affect the isotopic composition of the manufactured product. Therefore, one might speculate that products from different plants and even different batches might have characteristically different isotopic compositions. Given that the samples tested were identified only by their supplier, it is even possible that the same primary manufacturer made them all

CONCLUSION

Chlorine isotope compositions of chlorate and perchlorate can be determined to a precision as good as that achieved for standard chloride analysis (0.05‰, 2 × standard error of the mean). There are significant isotopic variations between the chlorate samples and perchlorate samples analyzed. In addition, there are also significant variations between crystals within the chlorate samples provided.

These differences between the measured isotopic compositions of chlorine in the samples analyzed, and the fact that they are different from the value expected of the feedstock chloride (~+0.09‰), suggest that the manufacturing process affects the isotopic composition of the product. Therefore, different samples may display a limited but significant range of characteristic isotopic compositions. However, from this limited survey, it is impossible to make a more conclusive statement.

The development of the method and the preliminary results are encouraging. The data suggest that there might be sufficient initial variation to be of value for forensic use. However, the limits of the range are small in comparison to the isotopic fractionations expected for microbial reduction and thus will also allow the method to be used to monitor extent of remediation of polluted water.

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